

# Diffusion of Pt dimers on Pt(111)

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We report the results of a density-functional study of the diffusion of Pt dimers on the (111) surface of Pt. The calculated activation energy of 0.37 eV is in *exact* agreement with the recent experiment of Kyuno *et al.* [Surf. Sci. **397**, 191 (1998)]. Our calculations establish that the dimers are mobile at temperatures of interest for adatom diffusion, and thus contribute to mass transport. They also indicate that the diffusion path for dimers consists of a sequence of one-atom and (concerted) two-atom jumps.

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## I. INTRODUCTION

The diffusion of adatoms — or very small clusters of them — on clean, infinite, defect-free surfaces remains, in spite of its conceptual simplicity, a largely unresolved problem. Experimentally, direct measurements of the trajectories of individual particles are possible (using field-ion microscopy) for only a few elements (notably Ir and Pt)<sup>1</sup> in a narrow range of temperatures. In most cases, the diffusivities are determined indirectly, e.g., by inferring them from island growth measurements (see for instance Ref. 2). The situation is just as difficult theoretically: though the diffusion constants can in principle be determined explicitly using, e.g., molecular-dynamics simulations, this is in practice extremely difficult because of computer and model-potential limitations.

The (111) surface of Pt is of particular interest. The diffusivity of adatoms has been measured using different approaches, and an activation barrier of 0.25-0.26 eV has been determined.<sup>3-5</sup> This is in disagreement with our first-principles result of 0.33 eV,<sup>6</sup> but within the error bar of a recent calculation by Feibelman,<sup>7</sup> which gives a barrier of 0.29 eV.<sup>8</sup> Though the agreement between theory and experiment can be judged satisfactory, questions remain concerning the role played by dimers in the kinetics of growth, and in particular the shape of islands as a function of temperature.

We have carried out a series of density-functional-theory calculations in order to determine the barrier and mechanism for diffusion of the Pt dimer on Pt(111). The activation energy we obtain — 0.37 eV — is in striking (and somewhat surprising) *exact* agreement with experiment.<sup>5</sup> Our calculations therefore indicate that the dimers are certainly mobile at temperatures of interest for adatom diffusion (and thus contribute to mass transport), as in fact can also be inferred from the measurements of Kyuno *et al.*<sup>5</sup> Our study reveals that the diffu-

sion path for dimers consists of a sequence of one-atom and (concerted) two-atom jumps.

## II. COMPUTATIONAL DETAILS

As already noted above, the calculations reported here were performed within the framework of density-functional theory.<sup>9</sup> Our previous studies of this surface<sup>6</sup> indicate that the local-density approximation (LDA)<sup>10</sup> to the exchange-and-correlation energy provides a better description of platinum than the generalized-gradient approximation (GGA);<sup>11</sup> the LDA was therefore used for all calculations reported here. The ion cores were approximated by pseudopotentials with 5*d* electrons treated as valence states. The pseudopotentials were generated using the semi-relativistic scheme of Troullier and Martins<sup>12</sup> and expressed in the Kleinman-Bylander form using the *s* component as the local one.<sup>13-15</sup> The electronic wave-functions were represented using a plane-wave basis set with kinetic energy up to 40 Ry. In order to improve convergence, the electronic states were occupied according to a Fermi distribution with  $k_B T_{el} = 0.1$  eV and the total energies obtained by extrapolating to zero electronic temperature. For similar reasons, the calculations were initiated using wave-functions obtained from the self-consistent solution of the Kohn-Sham Hamiltonian in a mixed basis set composed of pseudo-atomic orbitals and plane waves cut off at 4 Ry.<sup>16</sup> The minimization of the energy with respect to the electronic degrees of freedom was done using an iterative procedure.<sup>17</sup> After achieving electronic convergence, the atoms were moved according to a damped Newton dynamics until forces became less than 0.01 eV/Å. In view of the high energy cutoff needed in the plane-wave expansion, it is important to keep the system size to a minimum. To do so, we used a slab geometry consisting of four  $3 \times 3$  layers

(plus vacuum in the supercell approach) with the dimer adsorbed on one side. Only the top layer (plus the dimer) was allowed to relax. The  $\mathbf{k}$ -space integration was performed using a  $2 \times 2$  grid, the exact number of points depending on the actual symmetry of the configuration under consideration.

### III. RESULTS

#### A. Binding and dissociation energies

The binding energy of the dimer is given by  $E_{\text{binding}} = E_{\text{dimer}} + E_{\text{clean}} - 2E_{\text{adsorption}}$ , where  $E_{\text{dimer}}$  is the total energy of the system including the dimer,  $E_{\text{clean}}$  is the total energy of the system with a “clean” surface, and  $E_{\text{adsorption}}$  is the adsorption energy of a single adatom.

A single adatom on the (111) surface can sit either in a fcc site or in a (stacking-fault) hcp-like site. The latter lies 0.17-0.21 eV above the former in the case of platinum<sup>6,7</sup> i.e., is very unfavourable. For the equilibrium state of the dimer, one therefore expects the two atoms to sit in nearest-neighbour fcc sites, such as the  $f_1f_2$  configuration in Fig. 1. The corresponding configuration where the two atoms are in hcp-like sites, such as  $h_1h_2$ , indeed lies 0.30 eV above  $f_1f_2$ , we have verified. In both the  $f_1f_2$  and  $h_1h_2$  configurations, the dimer bond length is close to  $a/\sqrt{2}$  (with  $a$  the lattice parameter), the nearest-neighbour distance on the (111) surface. Other possible configurations of the dimer have longer or shorter bond lengths and are therefore unlikely. We have examined the  $f_1f_3$  configuration, where the dimer atoms are second nearest neighbours (bond length =  $\sqrt{3}a/\sqrt{2}$ ) and found it to lie 0.56 eV above  $f_1f_2$ . Likewise, the possible fcp-hcp configurations (such as  $f_1h_1$ ,  $f_1h_2$ , and  $f_1h_3$  — cf. Fig. 1) all lie substantially higher in energy than  $f_1f_2$ , as we will see below.

With the dimer in the  $f_1f_2$  configuration, we obtain a binding energy of 0.48 eV, with an error that we estimate to be of the order of 0.05 eV. This is much larger than the diffusion barrier for a single adatom, 0.33 eV.<sup>6</sup> The barrier towards dissociation is given, roughly, by the sum of the dimer binding energy and the diffusion barrier of the adatom<sup>18</sup> — 0.81 eV in the present case. We therefore expect the dimers to be stable, i.e., unlikely to dissociate, in the temperature range in which the adatoms are mobile. More precisely, the first step towards dissociation is most likely related to the  $f_1f_2 \rightarrow f_1h_3$  (rather than  $f_1h_2$ ) transition (from geometrical considerations: the  $f_1h_3$  distance is larger than the  $f_1h_2$  one; also, there are two recombination paths for  $f_1h_2$ , but only one for  $f_1h_3$ ). We find the barrier for this process to be about 0.75 eV, remarkably close to the above estimate.

#### B. Diffusion by successive jumps

We consider first the possibility that diffusion of the dimer proceeds by successive jumps of its constituent atoms. Referring to Fig. 1 again, we will assume that atom B, on the  $f_2$  site, jumps first, followed by atom A, on the  $f_1$  site. B can jump to either of the three adjacent hcp-like sites, as indicated by arrows in Fig. 1. The  $f_1h_i$  ( $i = 1, 2, 3$ ) configurations of the dimer are metastable states since hcp sites are not equilibrium sites on this surface. Evidently, these states will be relevant to diffusion only if they lie sufficiently low in energy above the equilibrium state — more specifically by an amount which is of the order of the barrier for single-atom diffusion (0.33 eV).

We have calculated the energies of the  $f_1h_i$  configurations of Fig. 1, and obtain, as measured with respect to the  $f_1f_2$  state,  $\Delta E = 0.87, 0.34$ , and 0.69 eV for  $f_1h_1$ ,  $f_1h_2$ , and  $f_1h_3$ , respectively. Thus, of the three possible intermediate configurations, only  $f_1h_2$  is probable on a timescale comparable to that for adatom diffusion (but of course cannot be excluded on longer timescales). We note that the *barrier* for the  $f_1f_2 \rightarrow f_1h_2$  process — 0.35 eV according to our calculations — is very close to the  $f_1h_2$  configurational energy; thus, the barrier for the  $f_1h_2 \rightarrow f_1f_2$  process is vanishingly small (an insignificant 0.01 eV) so that  $f_1h_2$  is very short-lived.

If diffusion proceeds via a sequence of single-atom displacements, then there are at this point two possibilities: (i) Atom A may jump to either  $h_1$  or  $h_4$ . (ii) Atom B may jump to either  $f_4$  or back to  $f_2$ . It is easy to see that, in either case, the next jump (of either A or B) would lead to an improbable high-energy state of type  $f_1h_1$  or  $f_1h_3$ , which both lie substantially above the equilibrium  $f_1f_2$  state. We can therefore only conclude that diffusion by successive single-atom jumps only brings about a local motion of the dimer, which is essentially trapped in a potential well (possessing multiple minima) out of which it cannot escape on a timescale appropriate to adatom diffusion.

We investigate next the possibility that diffusion proceeds via the concerted motion of the two atoms forming the dimer.

#### C. Diffusion by concerted jumps

In order to go from one equilibrium site (such as  $f_1f_2$ ) to another in a concerted manner, the dimer must go through a metastable near-neighbour hcp-hcp configuration, as evident from Fig. 1. As already noted above, the near-neighbour hcp-hcp configuration lies 0.30 eV above the equilibrium fcc-fcc state; this is comparable to the single-adatom diffusion barrier, and therefore is a possible candidate for the dimer diffusion path.

As depicted in Fig. 1, there exists three possibilities for such a concerted jump, labeled ‘ $cj_1$ ’, ‘ $cj_2$ ’, and ‘ $cj_3$ ’.

The paths ‘cj<sub>2</sub>’ and ‘cj<sub>3</sub>’ are equivalent by symmetry, but different from ‘cj<sub>1</sub>’: in the transition state of the cj<sub>1</sub> path, the two atoms forming the dimer sit on either side of a surface atom, which is not the case for cj<sub>2</sub> and cj<sub>3</sub>. This makes diffusion extremely difficult in the cj<sub>1</sub> direction; our calculations predict, indeed, a barrier of approximately 0.8 eV. In contrast, for the cj<sub>2</sub> (or equivalently cj<sub>3</sub>) process, we obtain a value of 0.37 eV. This is only 0.07 eV above the hcp-hcp configuration energy. Thus, once in this state, the dimer can easily jump to an adjacent equilibrium fcc-fcc configuration (which can be either the initial one or a new one) via the cj<sub>4</sub> or cj<sub>5</sub> process indicated in Fig. 1.

The barrier for the cj<sub>2</sub> process, 0.37 eV, is very close to that for adatom diffusion; though we have not calculated the corresponding prefactors (they are found experimentally to differ by roughly an order of magnitude),<sup>5</sup> it is therefore certainly the case that both processes will contribute significantly to diffusion at temperatures of interest. Kyuno *et al.*,<sup>5</sup> indeed, find the diffusivity of dimers at 150 K to be comparable to that of adatoms at 100 K, with a difference in activation barriers of 0.11 eV in favor of adatoms, larger than that observed here (0.04 eV). Following Bogicevic *et al.*,<sup>19</sup> the temperature at which an Arrhenius process becomes active can be estimated from  $T_0 = (E_A/k_B)/\ln(\nu_0/\Gamma)$  where  $E_A$  is the activation energy,  $\nu_0$  is the attempt-to-diffuse frequency (prefactor), and  $\Gamma$  is the actual frequency at which diffusion is taking place. For dimers,  $E_A = 0.37$  eV and  $\nu_0 \approx 1.6 \times 10^{12} \text{ s}^{-1}$  (using the prefactor determined experimentally);<sup>5</sup> with  $\Gamma \approx 1 \text{ s}^{-1}$ , corresponding to an experimental deposition rate of 0.001–0.1 monolayer per second, one finds that dimers become active at approximately 150 K.

It is important to note that if only cj<sub>2</sub>-type processes are possible, then (because the barrier for cj<sub>1</sub>-type processes is comparatively much larger) diffusion would be constrained to a one-dimensional corridor, consisting of a sequence of jumps such as cj<sub>2</sub>-cj<sub>4</sub>-cj<sub>2</sub>-cj<sub>4</sub>... Correlated jumps need not, however, be exclusive of other processes. In section III B, we argued that successive jumps *alone* would not lead to mass transport, which does not mean that they do not contribute. In fact, once in a hcp-hcp configuration, the dimer can find its way to another corridor by the combination of single-atom moves  $h_1h_2 \rightarrow f_1h_2 \rightarrow f_1f_2$ . The energies of the  $h_1h_2$  and  $f_1h_2$  configurations are comparable (0.30 vs 0.34 eV) and the barrier for the  $f_1h_2 \rightarrow f_1f_2$  process is a smallish 0.01 eV; this diffusion path is therefore highly probable. The corresponding barrier for the concerted  $h_1h_2 \rightarrow f_1f_2$  process is, we have just seen, 0.07 eV.

The error bar on the above values is of a few hundredths of an eV and we therefore cannot determine precisely which route will be the preferred one. It can however be safely concluded that either will lead to significant mass transport: the limiting factor for diffusion is the  $f_1f_2 \rightarrow h_1h_2$  barrier of 0.37 eV, quite comparable to that for single atoms.

## IV. CONCLUDING REMARKS

Direct measurements of the diffusion of Pt atoms and dimers on Pt(111) using low-temperature field-ion microscopy have been reported very recently by Kyuno *et al.*<sup>5</sup> The activation energy for adatoms is found to be  $0.260 \pm 0.003$  eV while it is  $0.37 \pm 0.02$  eV for dimers. The barrier for adatoms is in excellent agreement with previous experimental estimates,<sup>3,4</sup> which seems to rule out the possibility that the activation barrier for adatoms as deduced from growth experiments is “contaminated” by contributions from dimers.

For dimers, the measured barrier is in remarkable agreement with our theoretical estimate. Such a close agreement is probably to some extent fortuitous as our calculations are precise to no more than a few hundredths of an eV because of our neglect of dynamical and quantum effects, finite-size limitations, and the approximate character of the LDA. Nevertheless, the present study does establish that dimers are mobile at temperatures where single-atom diffusion is active and can therefore contribute to mass transport, albeit perhaps not in a very significant manner compared to adatoms. Our calculations, further, indicate that the pathway for dimer diffusion consists of a sequence of one-atom and concerted two-atom jumps. Such a diffusion mechanism has been reported recently in the case of Al dimers on Al(111) based on density-functional theory calculations (see Ref. cited in 8).

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- <sup>1</sup> For a recent review of diffusion coefficients obtained through FIM, see G. L. Kellogg, Surf. Sci. Reports **21**, 1 (1994).
- <sup>2</sup> J. A. Venables, Philos. Mag. **27**, 697 (1973).
- <sup>3</sup> M. Bott, M. Hohage, M. Morgenstern, T. Michely, and G. Comsa, Phys. Rev. Lett. **76**, 1304 (1996).
- <sup>4</sup> P. J. Feibelman, J. S. Nelson, and G. L. Kellogg, Phys. Rev. B **49**, 10 548 (1994).
- <sup>5</sup> K. Kyuno, A. Götzhäuser, and G. Ehrlich, Surf. Sci. **397**, 191 (1998).
- <sup>6</sup> G. Boisvert, L. J. Lewis, and M. Scheffler, Phys. Rev. B **57**, 1881 (1998).
- <sup>7</sup> P. J. Feibelman, Phys. Rev. Lett. **81**, 168 (1998).
- <sup>8</sup> As pointed out by A. Bogicevic (private communication), inclusion of zero-point vibrations is likely to lower the calculated barriers by about 0.02 eV; see for instance A. Bogicevic, P. Hyldgaard, G. Wahnström, and B. I. Lundqvist, Phys. Rev. Lett. **81**, 172 (1998).
- <sup>9</sup> P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- <sup>10</sup> D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- <sup>11</sup> J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
- <sup>12</sup> N. Troullier and J. L. Martins, Solid State Commun. **74**, 613 (1990); Phys. Rev. B **43**, 1993 (1991).
- <sup>13</sup> L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
- <sup>14</sup> X. Gonze, R. Stumpf, and M. Scheffler, Phys. Rev. B **44**, 8503 (1991).
- <sup>15</sup> M. Fuchs *et al.*, unpublished.
- <sup>16</sup> M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler, submitted to Computer Phys. Commun.
- <sup>17</sup> R. Stumpf and M. Scheffler, Computer Phys. Commun. **79**, 447 (1994).
- <sup>18</sup> M. C. Bartelt, L. S. Perkins, and J. W. Evans, Surf. Sci. Lett. **344**, L1193 (1995).
- <sup>19</sup> A. Bogicevic, J. Strömquist, and B. I. Lundqvist, Phys. Rev. Lett. **81**, 637 (1998).

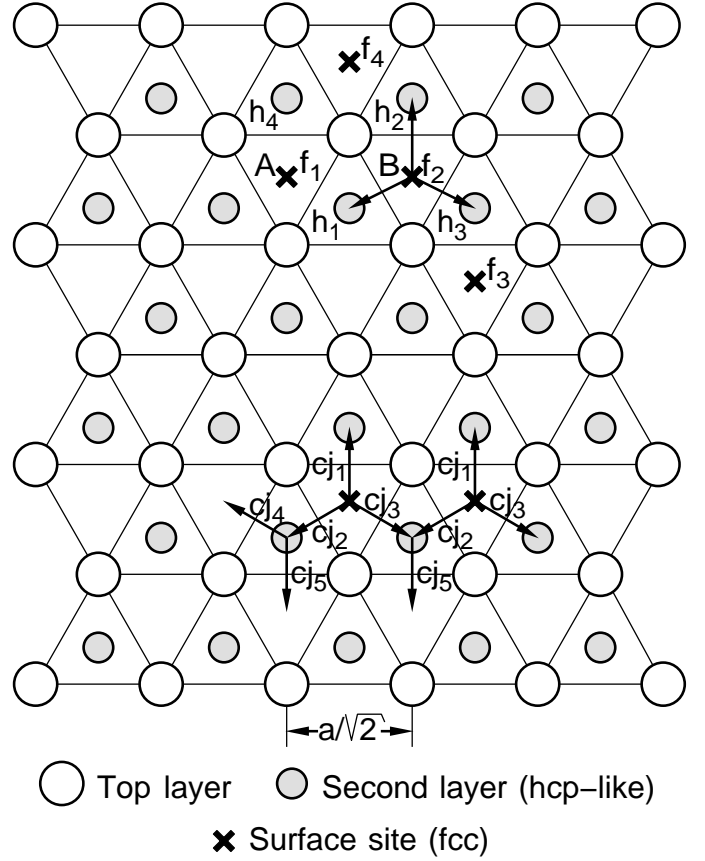


FIG. 1. The dimer diffusion processes studied in the present work; the symbols are explained in the text.